Photochemical separation of the isotopes H and D in an H_2CO-D_2CO mixture by the isotopic-filtration method

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The isotopic-filtration method was used to separate the isotopes H and D in the photolysis of an H_2CO-D_2CO mixture. The changes in the product ratio H_2/D_2 agree with the expectation that the reaction products are enriched by the isotope which is not contained in the filter cell.

The present study demonstrates the feasibility in principle of photochemical separation of isotopes with the aid of isotopic filtration of light. Insofar as we know, the attempts to employ this method have been mostly unsuccessful.[1,2]

The gist of the method is the following: Light from a continuous source passes first through a filter cell filled with isotopic molecules of one sort (A). The absorption of the light in this cell can be practically complete at wavelengths characteristic of the isotope A. The light entering the working cell, which is placed directly behind the filter cell, acts mainly on molecules having a different isotopic composition $'A$, so that only the molecules $'A$ react photochemically in the working cell. It is not essential to fill the filter cell with a substance of one isotopic composition. It is possible to use as a filter also a natural mixture of isotopes, provided their contents differ noticeably.

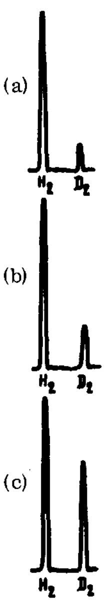
We tried the isotopic filtration method to separate the isotopes hydrogen and deuterium in the photolysis of formaldehyde in the gas phase. This system is convenient because it was previously used as an example to demonstrate the feasibility of photochemical separation of H and D at double the ruby-laser frequency.[3]

The photolysis was carried out with a DRSh-500 mercury lamp and cylindrical quartz cells 100 cm long and 3 cm in diameter. According to the published data,[4–6] the primary photolysis act in the region of $n-\pi^*$ absorption, depending on the wavelength of the light and the temperature, proceeds via two channels:

$$\text{I. } H_2CO \rightarrow H_2 + CO \quad \overset{T < 100^\circ C}{\lambda > 320\,\text{nm}} \quad \text{(molecular channel);}$$

$$\text{II. } H_2CO \rightarrow H + HCO \quad \overset{T > 100^\circ C}{\lambda < 320\,\text{nm}} \quad \text{(radical channel).}$$

In order for the reaction to proceed prodominantly via the molecular channel, the light of the lamp was passed through a glass filter that transmitted only wavelengths $\lambda > 320$ nm. The pressure of the H_2CO or D_2CO gas in the filter cell was maintained in the interval 50—150



Change of mass-spectrum intensities of the reaction products H_2 and D_2 as a function of the content of the filter cell: a) D_2CO, $P = 100$ Torr; b) empty filter cell; c) H_2CO, $P = 100$ Torr.

Data on the photolysis of an $H_2CO + D_2CO$ mixture.

Experiment No.	Filter	Pressure, Torr	Mixture composition $I_{H_2CO} : I_{D_2CO}$	Illumination time, min	Products[1)]		
					I_{H_2}	I_{D_2}	I_{H_2}/I_{D_2}
1	H_2CO	50	1.3	90	150	82	1.8
	–	–	–	25	105	27	3.9
	D_2CO	50	–	95	228	36	6.3
	–	–	–	20	109	28	3.9
2	D_2CO	100	1.3	240	123	25	4.9
	–	–	–	25	162	40	4.0
	H_2CO	100	–	210	186	121	1.5
	–	–	–	20	189	44	4.3
3	D_2CO	100	1.4	210	155	31	5.0
	–	–	–	20	200	54	3.7
	H_2CO	100	–	190	240	167	1.4
	–	–	–	20	101	24	4.0
4	H_2CO	150	1.1	240	100	68	1.5
	–	–	–	20	83	23	3.6
	D_2CO	150	–	210	194	28	7.0
	–	–	–	20	106	28	3.8
5	H_2CO	150	1.25	180	87	55	1.6
	–	–	–	30	151	40	3.8
	D_2CO	150	–	180	220	35	6.3
	–	–	–	30	104	27	3.8

1)Intensities of the mass-spectrum lines with a.m.u. = 2(I_{H_2}) and with a.m.u. = 4(I_{D_2}).

Torr at a temperature 150—180 °C. The working cell, filled with a mixture of the gases H_2CO and D_2CO in a ratio 1 : 1 with a total pressure 15—20 Torr, was at room temperature. The gases in the reaction mixture were analyzed out with the MKh-1303 mass spectrometer after first freezing out the unspent formaldehyde with liquid nitrogen.

We found CO, H_2, and D in the reaction products. The ratio CO : ($H_2 + D_2$) was close to unity. The HD admixture amounted to ~3% of the H_2 and D_2.

The figure shows the mass spectra of the products in the working cell for different filter-cell contents. The table lists the results of five experiments in which the working cell was alternately illuminated through filters with H_2CO or D_2CO. As a control, illumination through an empty filter cell was applied under identical conditions. The illumination time was chosen such that the degree of decomposition of the formaldehyde was the same in all the experiments.

It is seen from the table that the ratio H_2/D_2 of the products in the working cell varies strongly with the content of the filter cell. If the filter cell is empty, the average H_2/D_2 ratio amounts to 3.9 ± 0.1, which agrees with the analogous published data on the photolysis of an $H_2CO + D_2CO$ mixture.[4] In the case of illumination through a filter with H_2CO, this ratio is close to 1.6 ± 0.1, and in the case of a filter with D_2CO it is close to 5.9 ± 0.7.

The changes in the product ratio agree with the expected results, namely, the reaction products are enriched with the isotope not contained in the filter cell.

We have thus, obtained encouraging results on the use of the method of isotopic filtration for isotope separation.

[1]H. Hartley, A.O. Pender, E.J. Bowen, and T.R. Merton, Phil. Mag. 43, 430 (1922).

[2]W. Kuhn, M. Martin, and K.H. Eldau, Z. Phys. Chem. Abt. B15, 213 (1941).

[3]E.S. Yeung and C.B. Moore, J. Chem. Phys. 58, 3988 (1973).

[4]R.D. McQuigg and J.G. Calvert, JACS 91, 1590 (1968).

[5]A. DeGraff and J.G. Calvert, JACS 89, 2247 (1967).

[6]H.P. Sperling and S. Toby, Canad. J. Chem. 51, 471 (1973).